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Evaluation of an Inductively Coupled Plasma, Multichannel Spectrometric Analysis System

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An inductively coupled plasma, multielement atomic emission spectrometric analysis system has been evaluated with respect to the Environmental Protection Agency's need for a rapid method for determination of trace elemental concentrations in water. Data are presented on detection limits, curve fits and reproducibility of analytical curves, photomultiplier performance, dynamic range, reproducibility of analytical results, and stray light properties of the instrument.

The instrument as a whole performed well, but stray light arising from calcium and magnesium in typical hard waters caused significant errors at low concentration levels for a number of critical elements. Suggestions for reduction of the stray light and for empirical correction of its effects are discussed.

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EVALUATION OF AN INDUCTIVELY COUPLED PLASMA, MULTICHANNEL SPECTROMETRIC ANALYSIS SYSTEM

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FOREWORD

Nearly every phase of environmental protection depends on a capability to identify and measure chemical pollutants in the environment. The Analytical Chemistry Branch of the Athens Environmental Research Laboratory develops techniques for identifying and measuring chemical pollutants in water and soil.

A relatively new instrumental technique for the rapid, quantitative analysis of water for approximately two dozen trace elements utilizes inductively coupled plasma emission spectroscopy. This report presents an initial evaluation of one commercial instrument that embodies the technique.

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ABSTRACT

An inductively coupled plasma, multielement atomic emission spectrometric (ICP-MAES) analytical facility was evaluated with respect to the requirements of the Environmental Protection Agency for the determination of trace concentrations of the elements in water. Data are presented on detection limits, curve fits and reproducibility of analytical curves, photomultiplier performance, dynamic range, reproducibility of analytical results, and stray light properties of the instrument.

The instrument as a whole performed well, but stray light arising from calcium and magnesium in typical hard waters caused significant errors at low concentration levels for a number of critical elements. Suggestions for reduction of the stray light and for empirical correction of its effects are discussed.

This report was submitted in fulfillment of Contract No. EPA-IAG-D6-0417 by the Ames Laboratory under the sponsorship of the U.S. Environmental Protection Agency. This work covers the period June 24, 1974, to January 28, 1976, and work was completed June 17, 1976.

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LIST OF ABBREVIATIONS

ARL	-- Applied Research Laboratories
cm	-- centimeter
CRT	-- cathode ray tube
ICP	-- inductively coupled plasma
ICPQ	-- inductively coupled plasma quantometer
ICP-AES	-- inductively coupled plasma, atomic emission spectrometry
kW	-- kilowatt
l/min	-- liters/minute
MHz	-- megahertz
µg/l	-- microgram/liter
µl	-- microliter
mg/l	-- milligram/liter
mm	-- millimeter
mV	-- millivolt
nA	-- nanoampere
nm	-- nanometer
PVC	-- polyvinyl chloride
RF	-- radio frequency
RMS	-- root mean square
SD	-- standard deviation
sec	-- second
V	-- volt
W	-- watt

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SECTION 1

INTRODUCTION

To fulfill its environmental monitoring responsibilities, the EPA needs methods for the determination of elemental concentrations in a wide variety of natural and polluted waters. The nature of the water samples, the number of analyses required, and the need for reliable analytical data, often at very low concentration levels (1), dictate stringent requirements for an ideal analytical method. 1) The analytical method must have high powers of detection. 2) Potential sources of contamination (e.g. from sample pretreatment or concentration procedures) must be minimized. 3) Because 20 or more elements may need to be monitored in large numbers of samples on a routine basis, the method should be rapid and be able to determine the required elements simultaneously. 4) Because of the wide range of sample compositions that may be encountered in natural and polluted waters, the analytical method should possess minimal interelement or other matrix effects.

The ICP-AES method meets more of these requirements than any other technique (2, 3). The general properties of ICP methods have been described previously (3-8). The freedom from interelement effects of ICP-AES methods have been described by Larson, et al. (9).

This report summarizes the work performed in our laboratory on an ICP-AES system obtained for the Athens Environmental Research Laboratory, United States Environmental Protection Agency, Athens, Georgia. A detailed set of specifications (10) for and ICP-AES instrument, appropriate for the needs of the EPA, was prepared and along with a request for quotation was sent to all manufacturers (vendors) of such instrumentation. Two vendors responded with quotations. The analytical performances of the instruments from these vendors were then evaluated in the vendor's laboratories. On the basis of the quotations and the initial evaluations, a choice was made to purchase the Applied Research Laboratories (ARL) Inductively Coupled Plasma Quantometer (ICPQ). This instrument was tested at the Ames Laboratory for a period of about three months and was then transferred to the EPA Laboratory at Athens.

SECTION 2

CONCLUSIONS

An inductively coupled plasma, multielement atomic emission spectrometric analysis system has been evaluated with respect to the Environmental Protection Agency's need for a rapid method for determination of trace elemental concentrations in water. The data acquisition system of the ICPQ instrument in general performed well. The detection limit capabilities, the analytical curve fitting, the analytical curve reproducibility, and the photomultiplier performance approached the state-of-the-art for the types of equipment involved. A signal measuring system with a wider dynamic range capable of exploiting the wide range characteristics of the ICP would be desirable. A reduction in warm-up time of the system would also be desirable.

The most serious deficiency in the total system, however, is the polychromator in which high stray light levels may cause significant analytical errors, especially for such critical elements as arsenic, lead, and selenium.

With major reductions in stray light levels, the development of empirical methods for correction of the remaining matrix-related background changes, and improvements in nebulizer performance, all of which are presently feasible, the ICP-MAES technique is still the most practical approach for rapid multielement determinations of trace concentrations of the elements.

SECTION 3

RECOMMENDATIONS

The instrument under test for this evaluation required more than ½ hour warm-up time. A significant reduction of warm-up time would be desirable in future generations of these instruments, especially for short analytical sequences requiring only a fraction of an hour to several hours time.

Printout of the data is often the most time consuming part of the analytical procedure. For large sample loads a faster printer and disc virtual memory facilities should be considered.

A stepper-motor drive on the entrance slit profile screw of the polychromator would facilitate wavelength profiling on the instrument. This wavelength drive motor should be controlled by the system computer.

A CRT display with graphic capabilities would be helpful for rapid interpretation of wavelength profiles and other data.

Methods for improvement of the stray light properties of spectrometers need to be evaluated. Such methods include:

1. improved gratings (e.g. holographically recorded gratings),
2. better engineering of spectrometers including baffles, light traps, non-reflective coatings, and general optical design,
3. interference filters including narrow bandpass transmission and band rejection types.

The relative merits of stray light correction techniques need to be evaluated. These techniques include:

1. wavelength modulation,
2. wavelength profiles,
3. application of empirically determined interference correction factors or correction curves.

A reduction in clean-out time of the nebulization system would be useful especially when wide ranges in elemental concentrations may be encountered. Rapid methods for flushing of the sample uptake tube and nebulization chamber need to be considered.

A scanning monochromator would be a useful addition to the multichannel analysis system. The monochromator could be used as an alternate channel of variable wavelength and would be most useful if its analytical signals could be processed through one of the measurement channels of the multichannel system. The monochromator should also be usable as a scanning instrument for wavelength recordings.

SECTION 4

EXPERIMENTAL EQUIPMENT, SOFTWARE, AND PROCEDURES

APPARATUS

The main features of the analytical system consist of:

1. The ARL-1CPQ polychromator, equipped with 31 exit slits for the elements and wavelengths listed in Table 1. The grating is blazed for ≈ 300 nm. The polychromator covers the wavelength range 189.5 - 461.5 nm. Entrance slit, 12 μm; exit slits, 50 μm.

2. Plasma radio frequency (RF) power supply: Standard ARL unit, 27 MHz, 3 kW rating. The specifications required that the torch assembly be adjustable over its full vertical and horizontal range without change in the impedence match between the coupling box and the load coil. ARL accomplished this by combining the load coil and coupling box as a single movable unit.

   The considerable heat from the power amplifier section of the RF generator was exhausted through a fume duct in accord with ARL recommendations. Heat and gaseous products from the plasma source were also vented into the same hood system.

3. Sample generation and excitation hardware: The plasma torch, nebulizer, nebulization chamber (similar to Scott return flow type (5)), and gas flow control system were all standard items supplied by ARL. Nebulizer uptake tube: 60 cm of 0.75 mm i.d. polyethylene with a 50 μℓ capillary pipet attached to the intake end by means of a short section of heavy-walled PVC tubing. Liquid argon, supplied in cylinders containing 200 kg net argon, was employed for the plasma and nebulization systems.

Table 1. EPA QA 137 LINE ARRAY

Element		Wavelengths (nm)	
Ag	I	328.07	
Al	I	308.22	I 396.15
As	I	193.76	
B	I	249.68	
Ba	II	455.40	
Be	II	313.04	
C	I	247.86	
Ca	II	315.89	
Cd	II	226.50	
Co	II	238.89	
Cr	II	267.72	
Cu	I	324.75	
Fe	II	259.94	
Hg	I	253.65	
Mg	II	279.55	
Mn	II	257.61	I 403.08
Mo	II	202.15	
Ni	II	231.60	
Pb	II	220.35	I 405.78
Sb	I	206.84	
Se	I	196.09	
Sn	I	303.41	
Sr	II	407.77	
Ti	II	334.94	
V	II	292.40	
Y	II	242.22	II 371.03
Zn	I	213.86	

I Spectral line originates from neutral atom state.
II Spectral line originates from singly ionised state.

Number of elements	27
Number of wavelength	31
Atom lines	14
Ion lines	17

4. Data acquisition system:

Photomultipliers	Hamamatsu R300 series
Signal measurement technique	Capacitive time-integration of photocurrents
Minicomputer	DEC PDP 11/05
Data output	Teletype ASR 33 printed hardcopy with or without punched paper tape output.

SOFTWARE

Because of the copious data that can be generated by a rapid multielement analytical scheme such as the ICP-AES method, the computer software becomes a very important factor in the total system. Not only must the software produce correct analytical results from appropriate data, but it must supply cogent information about such things as system stability and analytical curves so that the analyst can quickly judge the quality of the data.

At the time the specifications were written for the EPA instrument, software packages available with commercial direct reading spectrometers were oriented largely for the needs of the iron, steel, and aluminum industries and, in our opinion, were not adequate for trace element analytical problems. More appropriate software capabilities were therefore specified for the EPA system. The specifications requested the following:

1. Ability to correct the reference standard and sample data for the blank contribution so that valid analytical curves could be established and accurate analyses could be performed. Merits of the various blank correction techniques have been discussed by Winge, et al.(2).

2. Option of printing blank corrected intensities with the concentration data in the analytical mode of operation.

3. Provision for weighting of calibration points to balance their relative influence on the determination of the analytical curve. This provision is particularly important for analytical calibration curves that cover greater than two orders of magnitude in concentration.

4. Ability to print analytical curve parameters, standard deviations of the curves, and residuals of the individual calibration points with respect to the curves.

5. Ability to gather "n" repetitive intensity measurements and to calculate average values and standard deviations from these data.

6. Ability to correct analytical data for interference contributions.

7. Ability to ratio analyte intensities to internal reference element intensities.

A second order, least squares curve fitting routine is employed for calculation of the analytical curves represented by the following equation

$$Y = A_0 + A_1X + A_2X^2 \qquad (1)$$

where Y = calculated concentration,
X = net measured intensity,
A_0 = intercept on the concentration or Y axis,
A_1 = slope of the curve at X = 0,
A_2 = coefficient of the second-order term.

Examples of analytical curve information from the ICPQ system will be explained later in Section 5. Theory of the analytical curve will be briefly described here.

Ordinarily an analytical curve should intersect the coordinate system very close to its origin. Intercept values (concentration axis) significantly larger than detection limits, either positive or negative, may be caused by improper blank corrections. Residual concentrations of elements in the reference standards cause negative intercepts, while contamination of the reference blank yields positive intercepts. Drifts in instrument sensitivity during the calibration procedure also may produce positive or negative deviations in an intercept, particularly if the calibration is based on a single initial reference blank determination.

The coefficient of the first order term, A_1, in Equation 1 corresponds to the slope at zero intensity and because it corresponds to concentration per unit intensity the instrumental sensitivity for an element increases as the slope decreases. If the analytical curve passes through or near to the origin of the coordinate system, then A_1 is effectively the slope at infinite dilution.

It is appropriate to note here that a weighting scheme was included in the curve fitting routine of the ICPQ software at our request. The weighting scheme, by minimizing relative concentration errors, produces analytical curves more appropriate for the wide dynamic range characteristics of ICP-AES methods.

Without weighting factors a wide-range analytical curve is determined largely by a few points at the high concentration end and large relative errors may result at the low concentration end of the curve.

The linearity of the analytical curves produced by the ICPQ system is characterized by the quantity L defined by

$$L = 1 - A_2X^2/y = A_0/y + A_1X/y. \qquad (2)$$

The latter equality in the above equation can be obtained directly from Equation 1. For a linear relation of the variables, $A_2 = 0$ and $L = 1$. For a nonlinear relation, L gives the fraction of the calculated concentration due to the linear elements (zero and first order terms) of the calibration curve equation.

OPERATING PROCEDURE

In general ARL recommendations were followed with regard to the starting and operating procedures.

Unless noted otherwise the following operating conditions were used:

RF forward power	1100 W indicated
Reflected power	≤2 W indicated
Plasma Ar	16 ℓ/min
Auxiliary plasma Ar	1.4 ℓ/m
Aerosol carrier Ar	1.0 ℓ/m
Integration period	10 sec

Observation zone in plasma limited to region approximately 13 to 17 mm above the load coil by a 4 mm vertical aperture at the entrance slit.

Photomultiplier voltage: Attenuator position 8-5 (≅ 750 V) was normally used for all channels unless high elemental concentrations in a sample series necessitated voltage reductions for specific channels.

Because a second order curve fitting routine is used, at least four reference standards should be used for calibration of the system. Four to six reference standards were normally used for studies involved in this evaluation. Also, because of the second order curve fit, analytical results outside of the calibrated range for any element should be checked carefully.

Cross contamination of solutions was minimized by immersion of the sample uptake tube in a dilute acid wash solution for a few seconds between samples or between sample and reference blank solutions.

WARM-UP TIME OF ICP

A significant bias in analytical results may be produced by insufficient warm-up time. On several occasions, even after the RF generator had been on for 40 to 60 minutes, relatively small changes in background levels during calibration caused significant errors at low concentration levels. On these occasions, however, the system had stabilized by the time analyses were begun, because periodic analyses of a reference standard over a several hour period yielded precision values approximating detection limit levels.

The stabilization process is shown by intensity-time profiles for three channels in Figure 1. These profiles and those from other channels not shown here suggest that the warm-up of the power supply and of the components in the plasma enclosure dominate the first portion of the curves, but that individual differences in the channels begin to appear in the latter portions of the curves. It should be noted that a computer smoothing process was employed for the plots in Figure 1 and that the ordinate scaling factors differ from plot to plot.

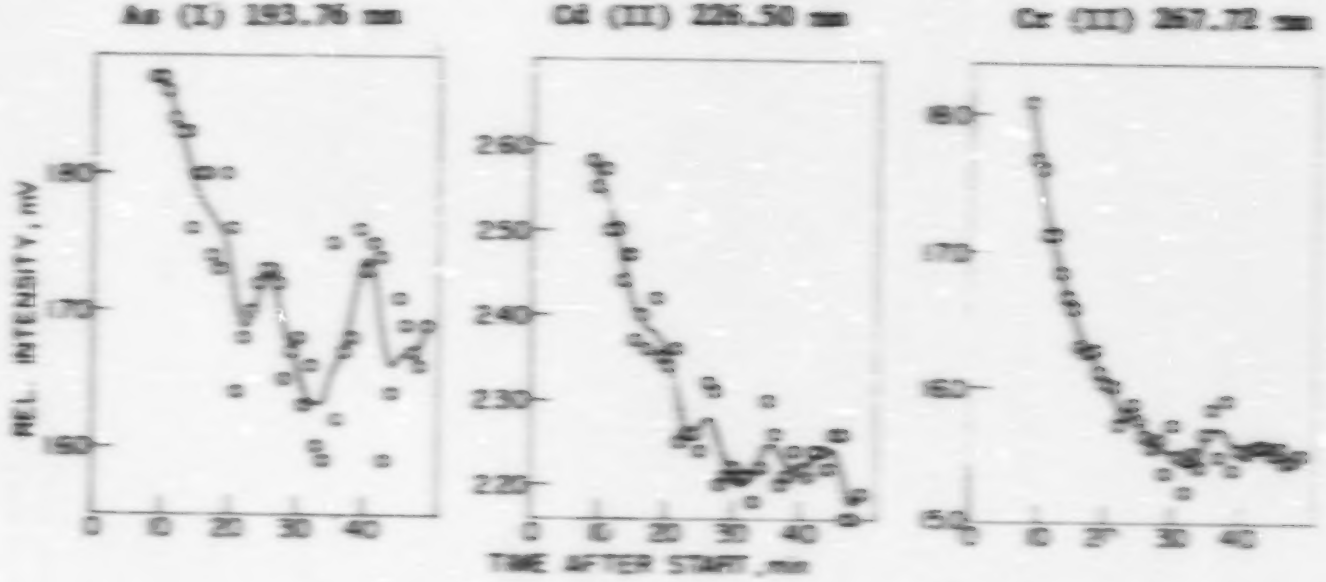

Figure 1. Examples of stabilization curves for deionized water background on ICP6.

SECTION 5

RESULTS

DETECTION LIMITS

Detection limits obtained periodically from the QA 13, system under several sets of operating conditions are shown in Table 7. The detection limit is defined as the analyte concentration equivalent to two times the standard deviation of the background beneath the analyte line. In general, if data from the same wavelengths are compared under the standard operating conditions (Condition Set V, Table 2), detection limits from the ICPQ system compare well with those obtained from other ICP systems in the Ames Laboratory (3). The significantly poorer detection limits obtained with Condition Set IV, without auxiliary plasma gas flow, are surprising because experience in our laboratory indicates this gas flow is usually not beneficial other than during the startup of the ICP.

PHOTOMULTIPLIER PERFORMANCE

Photomultiplier performance is a critical factor in the capabilities of a spectrometric analytical system such as the ICPQ.

Power Supply Stability

A commonly accepted criterion is that a photomultiplier high voltage supply should be a factor of ten more stable than the stability required of the photocurrent signal (11). Therefore, if 0.1% stability is expected in the photocurrent, the power supply should be stable to within 0.01%. The ICPQ photomultiplier power supply voltage was measured nine times (at one hour intervals) with a five-digit digital voltmeter. The results: The average value equaled -7.96 V ± 0.003%.

Dark Current

Photomultiplier dark current and the noise on the dark current may become significant in the measurement of very low signal levels. The specifications called for photomultiplier dark currents not to exceed 0.1 nA and relative standard

Table 2. DETECTION LIMITS (µg/l). ICP-QA 137 SYSTEM

		1	2	3	4	5	6	7	8
Ag	328.07	2	2	—	—	—	—	—	2
Al	308.22	—	80	60	40	120	20	20	20
Al	396.15	7	8	7	5	10	3	4	10
As	193.76	200	100	50	40	180	60	60	70
B	249.68	.8	.5	4	4	10	5	5	4
Ba	455.40	.3	.2	.2	.2	.6	.7	.5	.1
Be	313.04	.2	.2	.06	.4	.6	.2	.4	.4
Ca	315.89	4	2	1	8	10	6	20	10
Cd	226.50	3	2	1	3	10	.5	4	3
Co	238.89	3	4	2	3	7	4	4	2
Cr	267.72	6	6	2	3	1	5	2	4
Cu	324.75	1	1	2	.5	2	.7	1	2
Fe	259.94	2	2	1	1	10	2	210[a]	3
Hg	253.65	20	20	20	10	30	20	20	20
Mg	279.55	.1	.1	.6	1	?	.9	530[a]	.1
Mn	257.61	.5	.6	.3	.2	.5	.9	1	.3
Mn	403.08	10	8	6	1	2	9	.5	3
Mo	202.15	6	7	7	6	10	10	10	10
Ni	231.60	9	10	4	7	50	4	8	8
Pb	220.35	30	50	20	20	230	40	40	30
Pb	405.78	60	50	70	30	120	40	30	40
Sb	206.84	10	40	20	20	150	40	40	40
Se	196.09	40	60	20	60	380	50	50	40
Sn	303.41	70	80	80	50	120	80	60	60
Sr	407.77	.09	.04	.1	.03	.02	.9	.5	.05
Ti	334.90	10	10	6	3	10	6	5	5
V	292.40	.8	1	5	2	3	1	1	2
Y	242.22	5	5	4	10	30	30	10	20
Y	371.03	.4	.2	5[b]	3[b]	.3	.9	.6	.4
Zn	213.86	5	6	3	4	30	4	2	3

Table 1. Continued

Condition set[c]	I	I	II	III	IV	V	V	V
	ARL Sunland Ca 7/21/75	Ames Lab 9/10/75	Ames Lab 10/16/75	Ames Lab 10/16/75	Ames Lab 10/16/75	Ames Lab 12/4/75	Ames Lab 12/31/75	EPA Athens 1/26/76

[a] Very high concentrations of Fe and Mg had been run previous to the background measurements for this data set. The acid blank apparently scavenged deposits of these elements from the nebulizer, nebulization chamber or sample injection tube of the torch.

[b] For unknown reasons the standard deviation of the background for the V 371.03 nm channel was unusually high for these measurement sequences.

[c] Explanation of operating conditions.

	Condition Set				
	I	II	III	IV	V
RF power (W)	1600	1600	1100	1100	1150
Plasma Ar flowrate (l/min)	11	16	16	16	16
Auxiliary plasma Ar flowrate (l/min)	1.4	1.4	1.4	none	1.4
Aerosol Ar flowrate (l/min)	1	1	1	1	1
Observation height (mm)	20	18	18	18	15

deviations not to exceed 3% of the dark current for an integration period of 10 seconds (photomultiplier voltage at midrange or 750 V). The data in Table 3 show that none of the dark currents exceeded 0.1 nA (0.1 nA ≈ 1 mV) but that all of the standard deviations exceeded 3%. The latter problem is due predominantly to the uncertainties introduced by the measurement electronics rather than to noise on the dark current (see Section 5, Dynamic Range).

Detection Limits vs. Photomultiplier Voltage

Photomultiplier performance was measured in terms of detection limits as a function of applied voltage. Most of the photomultipliers yielded their best detection limits within the 700-800 volt range. The poorest detection limits obtained within the 630-950 volt range were often poorer by a factor of four or greater than those at the optimum voltage. These data were collected after the ICP had warmed up for one hour. The system was allowed to stabilize for 10 minutes after each voltage change before data were collected.

ANALYTICAL CURVES

Computer listings of data collected on a typical set of analytical curves generated by the ICPQ system are shown in Tables 4 and 5. The curve coefficients and root mean square (RMS) error data can be retrieved from storage at any time by a simple keyboard command as can the error table data. The former were usually retrieved immediately after a calibration was completed. The individual element error tables were usually not printed until the end of a run or the end of a day because approximately 30 minutes printing time was required for 30 channels.

As noted in Section 4, under ordinary circumstances the intercept values for the analytical curves should be very small. The data in Table 4 show, for example, that the intercepts are usually at detection limit levels or below. The A_0 column yields base solution concentrations directly when samples are analyzed by the standard addition technique, that is, if valid blank corrections have been applied.

The RMS error data in Table 4 are calculated from the concentration and intensity residuals* and pertain only to the

*An intensity residual is the difference between a measured intensity and the intensity derived from the analytical curve for a given concentration. A concentration residual is the difference between the concentration calculated from the analytical curve and the concentration assigned to the reference standard.

Table 3. PHOTOMULTIPLIER DARK CURRENT DATA[a]

	Ave. Value (mV)	% SD		Ave. Value (mV)	% SD		Ave. Value (mV)	% SD
Ref[b]	5199.	0.0106	Ag	0.1250	29.75	Al	0.2630	22.15
Ac	0.4190	11.33	As	0.1940	12.90	B	0.0290	61.79
Ba	0.1920	14.06	Be	0.0629	42.36	[illegible]	0.4179	6.841
Ca	0.3020	9.208	Cd	0.0470	34.81	Co	0.1220	6.835
Cr	0.1259	18.46	Cu	0.2009	12.94	Fe	0.1249	25.36
Hg	0.0130	162.3	Mg	0.1660	18.00	Mn	0.6369	10.09
Mo	0.1890	14.20	Nb	0.1989	11.47	Ni	0.0279	116.3
Pb	0.1160	23.41	Pb	0.3359	12.24	Sb	0.0200	102.7
Se	0.1740	27.38	Sn	0.0270	100.3	Sr	0.0599	35.13
Ti	0.3489	10.32	V	0.3040	15.05	Y	0.0699	46.16
W	0.2689	10.28	Zn	0.3979	5.530			

[a]Average values and precision data obtained from ten consecutive ten-second integrations of the dark current.

[b]Reference channel (Ref) for which the input signal is derived directly from the photomultiplier high voltage supply.

Table 4. EXAMPLES OF ANALYTICAL CURVE COEFFICIENTS AND ERROR DATA

Channel	RMS Error: Concentration mg/l	RMS Error: Intensity mV	Curve Coefficients: A_2 mg/l(mV)$^{-2}$	A_1 (slope) mg/l(mV)$^{-1}$	A_0 (intercept) mg/l
As	0.051360	0.078687	0.16543269E -3	0.662933	-.024166
B	0.007892	0.038986	0.19538216E -4	0.050018	-.002081
Ba	0.003180	2.23229	0.10950316E -7	0.001440	-.000084
Be	0.000698	1.56750	0.32466687E -8	0.000435	-.000076
Ca	0.004666	0.112328	0.19574508E -4	0.943164	-.000757
Cd	0.002189	0.056116	0.15552156E -4	0.039947	-.001562
Co	0.039864	1.50954	0.70346869E -6	0.027913	-.003232
Cr	0.021290	1.91339	0.68437657E -6	0.012182	-.001634
Cu	0.008293	1.68516	0.17270213E -6	0.005290	-.000992
Fe	0.049013	1.81559	0.73030443E -5	0.028390	-.005492
Hg	0.211414	0.364180	0.59943646E -4	0.192077	-.017605
Mg	0.078167	13.2167	0.27351234E -7	0.001420	-.001267
Mn	0.011354	4.33669	0.37298378E -7	0.002777	-.000193
Mo	0.640617	1.66851	0.14189282E -5	0.013123	-.003429
Na	0.023022	0.584106	0.66141365E -6	0.040216	-.008370
Ni	0.108347	1.77932	0.56251884E -5	0.056741	0.001007
Pb	0.034863	0.886066	0.52168965E -3	0.458038	-.025443
Pb	0.019660	0.877925	0.18452108E -3	0.268478	-.013218
Sb	0.019597	0.638085	0.32751262E -3	0.524383	-.008967
Se	0.015647	0.834128	0.48753619E -2	0.474166	-.006567

Table 5. EXAMPLES OF INFORMATION GIVEN FOR THE INDIVIDUAL CALIBRATION POINTS FOR EACH ANALYTICAL CURVE

	Std. No.	Conc. mg/L	Int. mV	Conc. Res. mg/L	Int. Res. mV	L
Be	01	0.003999	8.72314	0.000048	0.106238	0.999938
Error	02	0.012000	26.9501	-.000264	-.579433	0.999803
Table	03	0.040000	85.9335	0.000821	1.80482	0.999400
(Be 313.04 nm)	04	0.119998	264.859	-.000964	-2.12298	0.998102
	05	0.399993	873.187	-.000541	-1.29275	0.993811
	06	2.00000	4255.50	0.000954	2.22762	0.970602
Mo	01	0.099998	2.56318	0.004057	0.101154	0.999955
Error	02	0.300003	7.66674	0.000005	0.000129	0.999870
Table	03	1.00000	25.5000	-.017579	-.437478	0.999569
(Mo 287.15 nm)	04	3.00000	74.5117	0.008101	0.201548	0.998775
	05	10.0000	246.875	0.039623	0.993333	0.995968
	06	50.0000	1219.87	-.034912	-.904414	0.980315
Pb	01	0.099998	0.286666	-.005905	-.012901	0.999571
Error	02	0.300003	0.713348	-.001560	-.003411	0.999115
Table	03	1.00000	2.18994	0.019864	0.043585	0.997498
(Pb 220.35 nm)	04	3.00000	6.54321	0.006065	0.013442	0.992554
	05	10.0000	21.5968	-.066816	-.153390	0.975869
	06	50.0000	98.1406	0.048578	0.136593	0.899506

calibration curves. Sample analyses performed after calibration may be subject to additional errors which cannot be estimated from the analytical curve data. Because the RMS error values in Table 4 do not apply to specific concentrations or intensities, we feel that relative residuals provide a better basis for calculation of the uncertainty in a calibration curve. A relative residual is the absolute residual divided by the measured or assigned value for each calibration point. Expressed as a percentage the resulting relative RMS or standard error would then provide an estimate of the error associated with any point on the calibration curve.

The concentration and intensity residuals in Table 5 show that the calculated curves fit the calibration points very closely. If a concentration error has been made in a reference solution it will produce relatively large residuals. The *L* values for the beryllium and molybdenum calibrations in Table 5 show that the deviations of these points from a linear relation with concentration are hardly significant. The lead data show a more significant deviation from linearity. If self-absorption is the cause of the non-linearity, then the L values will naturally decrease with increasing concentration. In all of the calibrations performed with the ICPQ system, very few calibration points had L values less than 0.85-0.90. Most had L values in the 0.97-1.0 range.

DYNAMIC RANGE

Utilisation of the wide dynamic range capabilities of the ICP excitation source (5, 12) naturally requires wide dynamic range in the signal measurement system. The ICPQ readout system has an absolute dynamic range of 0.01-10,000 mV. The practical dynamic range is limited, however, by the noise characteristics of the signal processing electronics. For example, with a 10 mV signal, the electronics contributed an uncertainty of about ± 0.5% while at 1 mV the uncertainty was ± 3-4%. If ± 1% uncertainty is accepted as a reasonable objective for analytical results, then the practical dynamic range of the ICPQ is limited to 3-3½ orders of magnitude. The concentration interval to which this practical dynamic range applies can be shifted moderately, of course, by changes in photomultiplier voltage.

Examples of analytical curve data for a four decade range test are shown in Table 6. In general, these data indicate that acceptable curve fits, intercepts, and linearity factors have been achieved. The linearity factors must be interpreted with respect to the highest reference standard concentrations which for the data in Table 6 range up to a factor of 10^6 above the detection limits.

Table 6. EXAMPLES OF DATA FROM ANALYTICAL CURVES COVERING A FOUR DECADE RANGE IN CONCENTRATION[a]

Channel	RMS Error		Curve Coefficients		
	Conc. mg/l	Int. mV	A_2 mg/l(mV)$^{-2}$	A_1(slope) mg/l(mV)$^{-1}$	A_0(intercept) mg/l
Mn	0.144782	7.21684	2.38426E-7	0.022893	0.002720
Cu	0.036428	3.44151	7.67108E-8	0.011191	0.001990
Al	0.141287	2.45126	2.25548E-7	0.058717	0.006106
Mn	0.063146	2.24173	1.31148E-7	0.028729	0.001168

	Std. No.	Conc. mg/l	Int. mV	Conc. Res. mg/l	Int. Res. mV	r
Mn 257.61 nm	01	0.024999	0.959991	0.000300	0.013141	1.000002
	02	0.250000	10.9299	-.003664	-.160112	0.999885
	03	2.50000	108.988	-.000645	-.028245	0.998867
	04	25.0000	1070.18	0.230663	10.1988	0.985078
	05	250.000	9939.00[b]	-.227136	-12.4226	0.905962
Cu 324.75 nm	01	0.010000	0.660003	0.000622	0.055632	0.999997
	02	0.099998	8.91015	-.001718	-.153587	0.999939
	03	1.00000	89.3710	-.022743	-.245385	0.999387
	04	10.0000	883.375	0.060111	5.42731	0.994014
	05	100.000	8514.00	-.054871	-5.44771	0.964394

Table 6. Continued

	Std. No.	Conc. mg/l	Int. nV	Conc. Res. mg/l	Int. Res. nV	r
Al	01	0.049999	0.609985	0.006075	0.103470	0.999998
396.15	02	0.500000	8.62011	-.014269	-.243025	0.999966
nm	03	5.00000	85.0390	-.002284	-.038924	0.999674
	04	50.0000	846.062	0.226162	3.86519	0.996771
	05	500.000	8374.00	- 219779	-3.87718	0.968368
Mn	01	0.024999	0.649993	0.005157	0.179520	0.999998
403.08	02	0.250000	8.87988	-.004287	-.218857	0.999959
nm	03	2.50000	87.4218	-.013255	-.461588	0.999599
	04	25.0000	864.750	0.105510	3.68725	0.996077
	05	250.000	8537.00	-.092536	-3.35296	0.961770

[a]Operating conditions as in Set 1, Table 2.

[b]This intensity value is very close to the upper limit of the digital voltmeter and, in fact, may have reached the actual readout limit.

REPRODUCIBILITY OF CALIBRATION

Reproducibility of calibration curve data produced by the ICPQ system was determined before and after delivery to the Ames Laboratory. The data shown in Table 7 were obtained from nine independent calibrations of the Zn channel, one each hour for an eight hour period. Five reference standards (0.03, 0.1, 0.3, 1.0, and 3.0 mg/L Zn) were used for each calibration procedure. The data show that the day-long stability of the Zn channel was much better before than after delivery. The poorer stability after delivery was due to a rather constant drift in the curve coefficients rather than to random variation. This drift has not been explained but subsequent analytical measurements on the zinc channel did not show drift to be a serious problem. The 1000% relative standard deviation for the intercept, before delivery, is not considered significant because this value corresponds to a concentration equivalent of only about two times the detection limit for zinc.

SHORT TERM REPRODUCIBILITY

The authors consider the short term stability (over one-half to one day periods) more important than day-to-day repeatability because complete recalibration with four to six reference standards can be accomplished in little more time than is required for triplicate analyses of a single standard for restandardisation. For this reason we did not request that a restandardisation provision be included in the software.

Table 8 shows an example of short term stability obtained from a reference standard that was run 10 times at approximately equal time intervals throughout a normal analytical sequence. During this sequence 12 blank determinations were made and 38 ground and surface water samples from an Iowa Coal Project mine site were analyzed. The reference standard was one of the series of standards used in the initial calibration. The reference standard elemental concentrations included the approximate ranges found in the mine site samples. The total elapsed time from the beginning of the calibration to completion of the sample analyses was about three hours. No adjustments of system parameters were made during this period.

The average values and standard deviation data for most of the elements in Table 8 show adequate stability for most trace element analytical work. Also the results of the individual analyses showed that most of the variation was random in nature without evidence of drift. The average values for lead and antimony, however, show greater errors than expected. These errors may have been caused by errors in reference standard concentrations or by lack of stability in these channels during

Table 7. REPRODUCIBILITY OF CALIBRATIONS FOR THE Zn 213.86 nm CHANNEL BEFORE AND AFTER DELIVERY OF THE ICPQ SYSTEM TO THE AMES LABORATORY[b]

	Before Delivery		After Delivery	
	Ave. Value[a]	% RSD	Ave Value[a]	% RSD
A_2 (mg/l per mV^2)	-0.5×10^{-6}	± 46%	$-.1372 \times 10^{-5}$	± 51.2%
A_1 (Slope).(mg/l per mV)	0.00785	± 0.70%	0.009830	± 3.57%
A_0 (Intercept).(mg/l)	-0.0504]	± 1000%	0.0193	± 47.9%
Ekdg (mV)	85.7	± 1.07%	81.2	± 1.74%

[a]Average of nine individual measurements.

[b]Operating conditions were as Set I, Table 2.

Table 8. REPRODUCIBILITY OF ANALYTICAL DATA FROM A "REFERENCE STANDARD" RUN AT REGULAR INTERVALS DURING A NORMAL ANALYTICAL SEQUENCE

		Reference standard (ug/l)	Measured average (ug/l)	Standard deviation (ug/l)
Al	308.22	1000	984	± 17
Al	396.15	1000	1000	66
As	193.76	200	193	44
B	249.68	200	199	6.8
Ba	455.40	200	201	1.4
Be	313.04	2	2.1	.09
Co	238.89	100	101	2.9
Cr	267.72	20	19	2.5
Cu	324.75	20	20	.6
Fe	259.94	4000	3950	38
Hg	253.65	200	197	13
Mn	257.61	200	196	2.3
Mo	403.08	100	106	6.2
Ni	231.60	100	105	5.4
Pb	220.35	200	283	31
Pb	405.78	200	232	10
Sb	206.84	200	241	22
Sn	303.41	200	229	23
Sr	407.77	2000	2030	11
V	292.40	20	23	1.2
Y	371.03	20	21	.4
Zn	213.86	1000	1020	16

the calibration process (see discussion of warm-up time, Section IV).

STRAY LIGHT

With respect to the determination of trace elemental concentrations the stray light characteristics of the ICPQ polychromator constitute its most serious deficiency. Calcium and magnesium, because of their very intense ion lines emitted in the ICP, are the most common elemental sources of stray light, although other elements may contribute stray light if present at high concentrations. The general subject of the effects of stray light on the spectroscopic determination of ultratrace concentrations of the elements has been discussed by Larson, et al (13).

Three main instrumental sources of stray light have been identified in the ICPQ polychromator: 1) grating scatter, 2) reflections and scatter in the secondary optics, i.e. the region between the exit slits and the photomultipliers, and 3) general scatter from reflections by internal surfaces of the polychromator.

Examples of stray light, due predominantly to grating scatter, are shown by the wavelength profiles in Figures 2 and 3. These profiles were obtained by stepwise movement of the entrance slit along the Rowland circle thereby changing the angle of incidence of the source radiation on the grating. A small wavelength interval (±0.1 nm for the profiles in Figures 2 and 3) thus sweeps past each exit slit. The chromium profile in Figure 2 shows that a typical hard water matrix (150 mg/ℓ Ca and 40 mg/ℓ Mg) elevates the background beneath the line an amount equivalent to about 11 µg/ℓ chromium. Similarly, the antimony profile in Figure 2 shows a background elevation equivalent to 200 µg/ℓ antimony. Figure 3 shows wavelength profiles of the Cd 226.50 nm region obtained from four real water samples. The background elevations correlate closely with the calcium and magnesium concentrations measured in these samples as shown in Table 9.

Secondary optics stray light should not be a significant factor in the profiles in Figures 2 and 3 because the Mg 279.55 nm exit slit was blocked and no exit slits were present for the very strong calcium lines. The profiles discussed above, as well as other profiles not shown here, suggest that stray light causes problems throughout the whole useful wavelength range of the polychromator.

Figure 4 illustrates the secondary optics stray light problem in the QA 137 system. Separate profiles were obtained for each spectral line from deionized water and from 1000 mg/ℓ

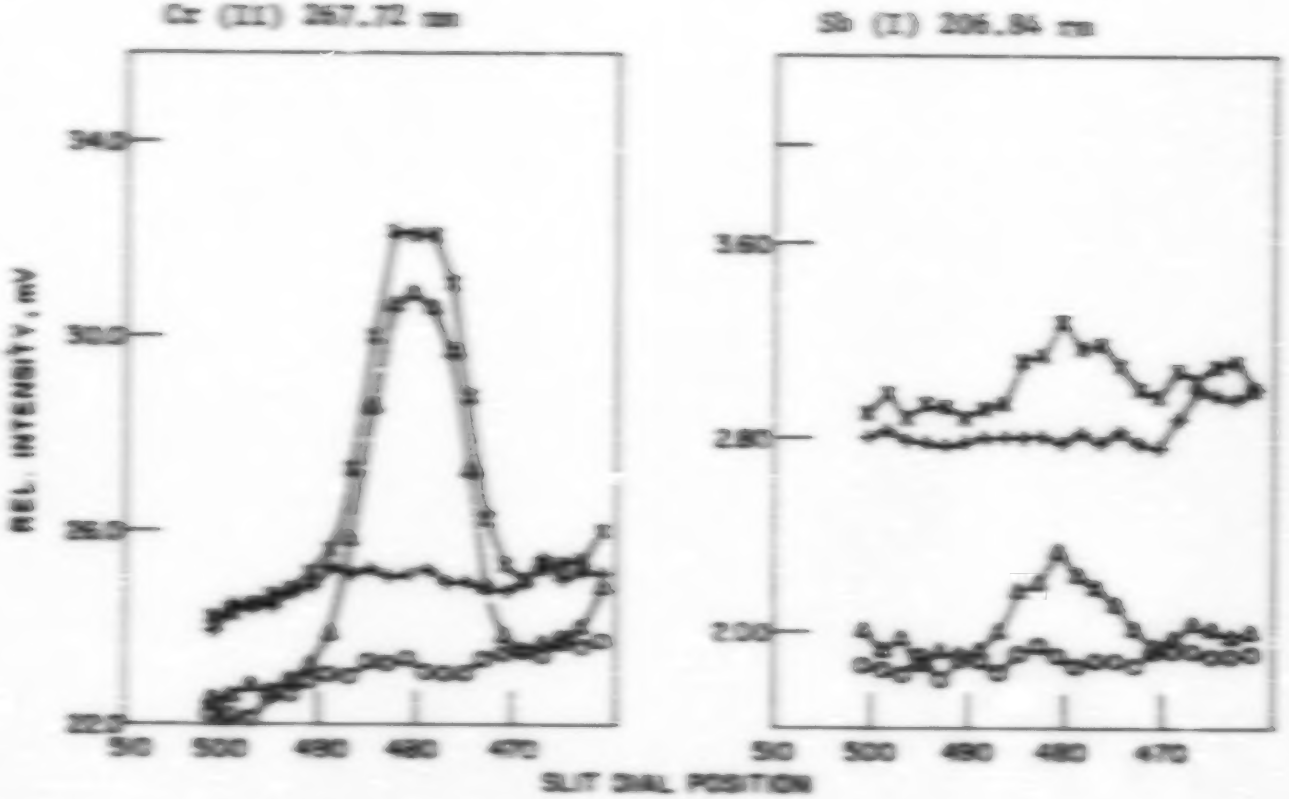

Figure 2. Examples of wavelength profiles that show the effects of stray light caused by concentrations of calcium and magnesium typical in hard water. 0 deionized water, Δ analyte mixture containing 50 μg/ℓ Cr and 100 μg/ℓ Sb, + hard water matrix (150 mg/ℓ Ca, 40 mg/ℓ Mg), X analyte mixture as above in hard water matrix.

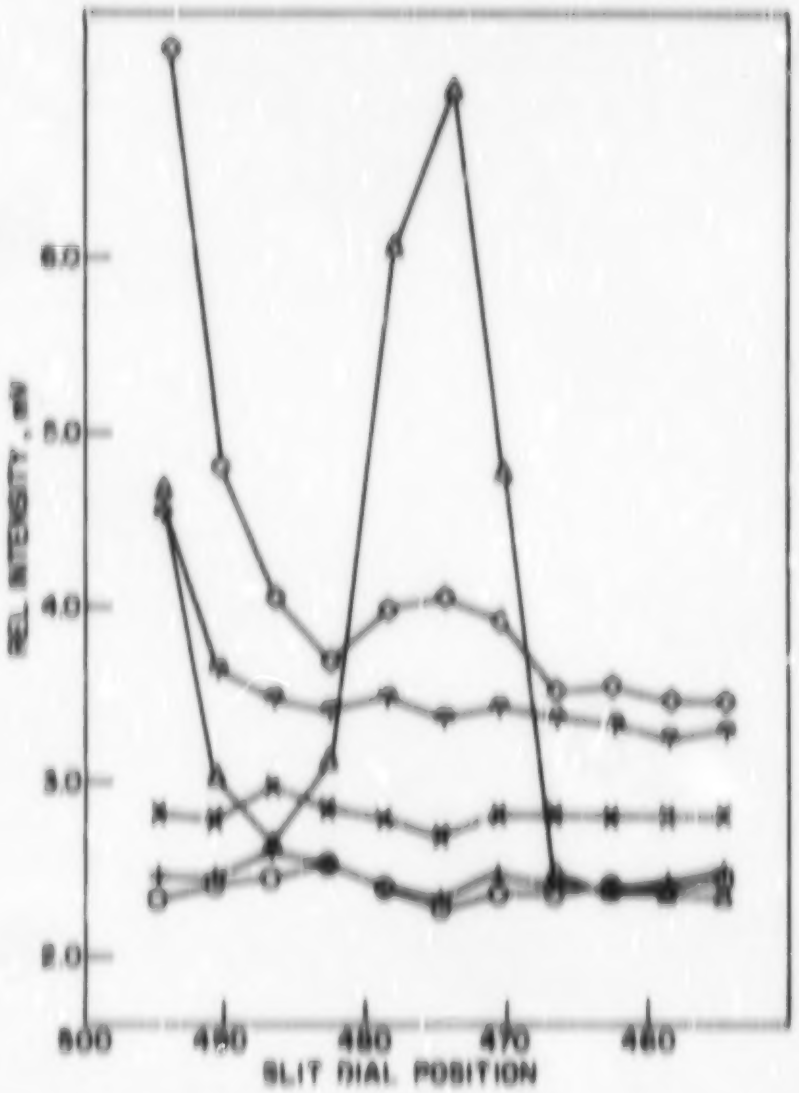

Figure 3. Wavelength profiles of the Cd 226.50 nm line. The profiles were obtained from four surface water samples containing different concentrations of calcium and magnesium (see Table 10). O deionized water, + Scott Pond, X Site 10, ◇ Site 21, ✱ Site 53, Δ 200 µg/L Cd reference standard.

Table 9. MEASURED CALCIUM AND MAGNESIUM CONCENTRATIONS FROM FOUR SURFACE WATER SAMPLES FOR WHICH WAVELENGTH PROFILES OF THE Cd 226.50 nm REGION ARE SHOWN IN FIGURE 3

Sample identification	Concentration (mg/l)	
	Ca	Mg
Scott Pond	10	4
Site 10	160	26
Site 21	290	140
Site 53	220	90

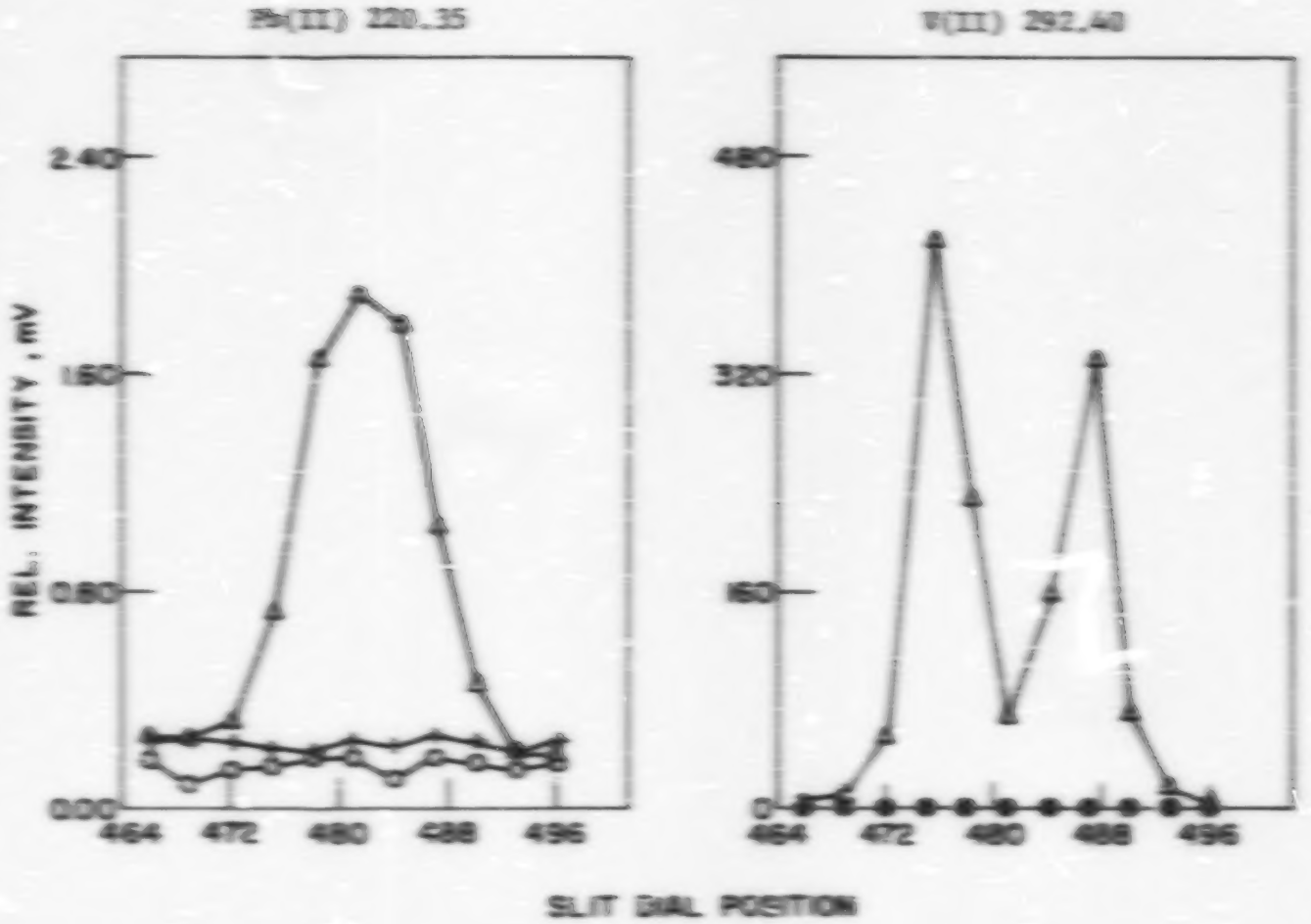

Figure 4. Examples of stray light arising in the secondary optics region of the GA 137 polychromator. All exit slits were blocked except that for the Hg 279.55 nm line. ○ deionized water, △ 1000 mg/L Mg, + 1000 mg/L Ca.

calcium and magnesium solutions. All slits except the Mg 279.55 nm slit were blocked with opaque flat black paper. The pseudo line profiles that occur as the magnesium line traverses its slit must therefore result from scattering of the magnesium radiation to the detectors of the other elements. Secondary optics scattering of the magnesium wavelength was observed for 14 of the 19 spectral lines between and including the Pb 220.35 and Ti 334.90 nm lines. In general, the secondary optics stray light becomes more severe near the magnesium wavelength, but as Figure 4 shows, it is still significant as far away as the Pb 220.35 nm wavelength. Geometrical relations between the secondary mirrors and photomultipliers determine which channels pick up the most stray light. The geometrical complexity of the secondary optics region of the GA 137 polychromator (with the spectral line array as listed in Table 1) is shown in Figure 5.

Sources of stray light other than the grating and secondary optics are also present in the GA 137 polychromator. Examples of such stray light are shown by the profiles in Figure 6 which were obtained simultaneously with the profiles in Figure 4 (all slits blocked except Mg 279.55 nm). The barium and selenium wavelengths are near the extreme ends of the wavelength range of the GA 137 polychromator and do not show evidence of secondary optics stray light (Peaks corresponding to the traverse of the magnesium line across its slit are not apparent). Instead, the calcium and magnesium solutions cause a general elevation of the background due to scattering from various internal surfaces of the polychromator. This general stray light from 1000 mg/L calcium corresponds to a few times the detection limits for barium and selenium (see analytical curve slope data in Table 4).

Stray light levels have been quantified for 38 wavelengths on the GA 137 spectrometer as shown in Tables 10 and 11. To obtain these data the system was calibrated for all elements listed in the table. The several calcium and magnesium concentrations were run as samples with a 1% HNO_3-deionized water solution as the reference blank. The net sample signal was then converted to an equivalent concentration for each analyte element. The same measurement sequence was performed at the analyte line wavelengths and at 0.04 nm intervals above and below these wavelengths (new reference blank values were established for each of the offset wavelengths). In general the data show a high degree of internal consistency. If the concentration equivalents are significant with respect to the detection limits and if the three values within a set are reasonably consistent then stray light is most probably involved. If the concentration equivalents within the -0.04, 0, and +0.04 nm set differ by more than a few times the detection limit, three possible causes are suggested:

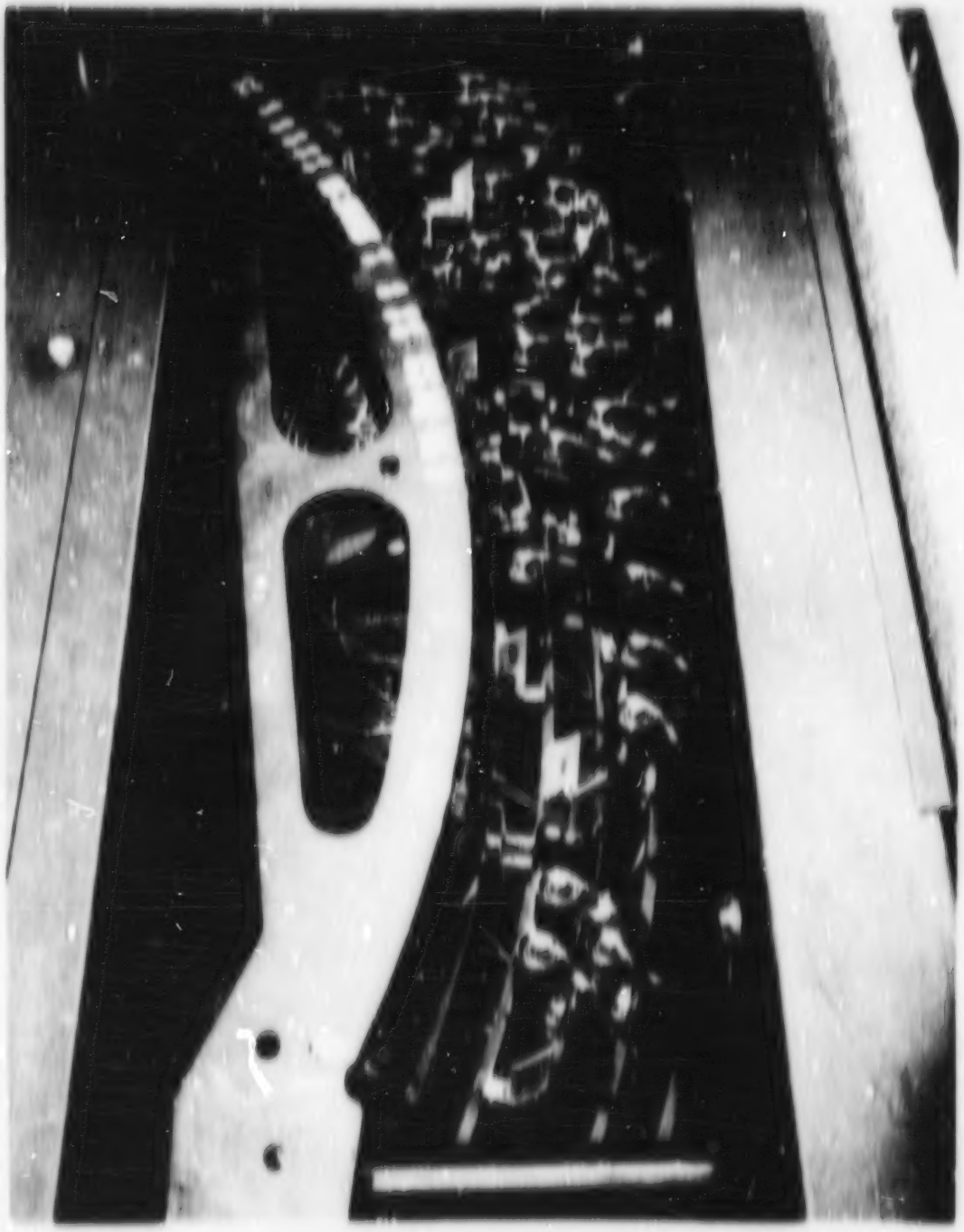

Figure 5. The secondary optics region of the GA 137 polychromator showing the exit slit frame, the secondary mirrors and photomultipliers.

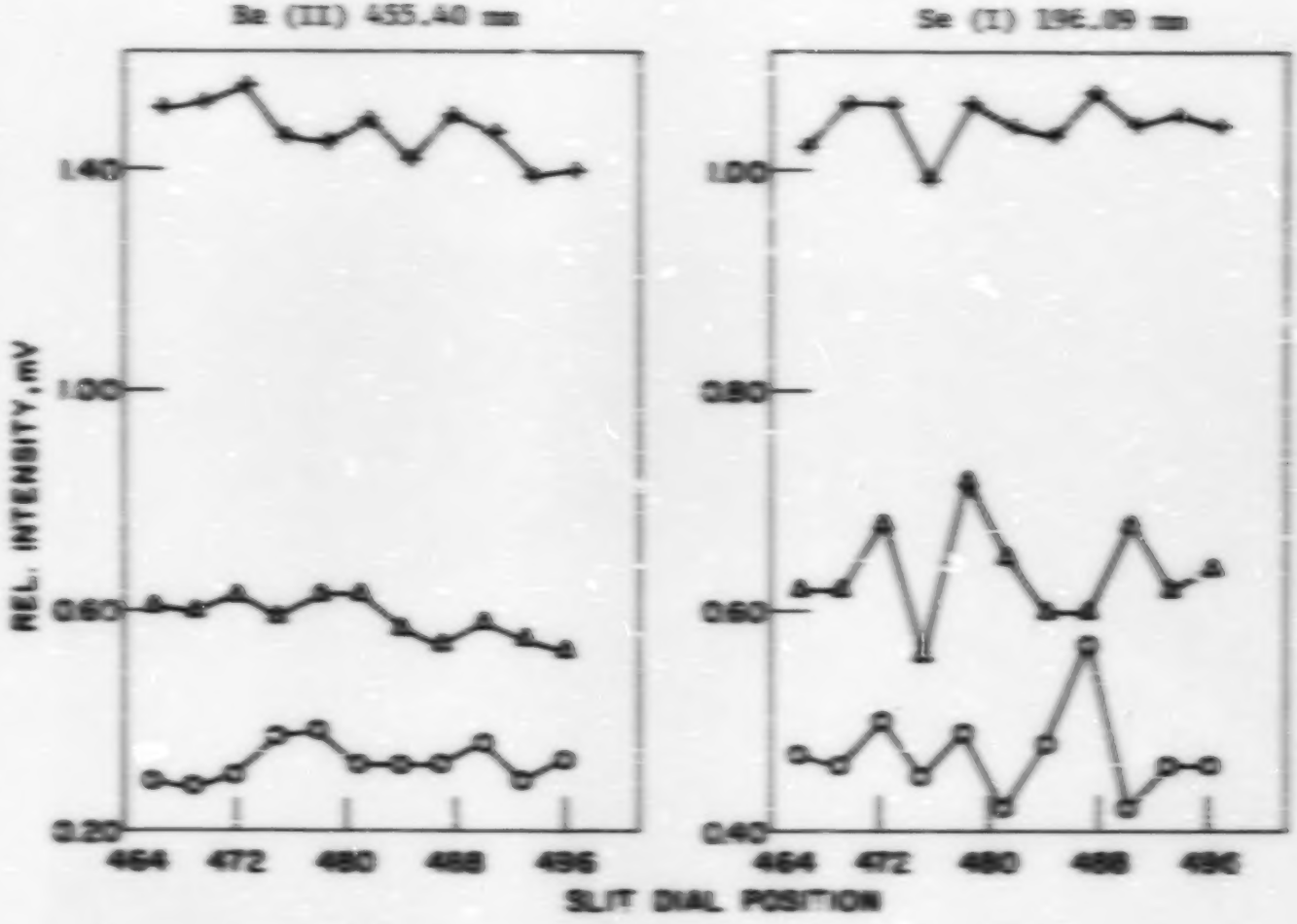

Figure 6. Examples of general stray light arising from general scattering within the polychromator enclosure. All exit slits were blocked except that for the Hg 279.55 nm line. Curve symbols same as on Figure 4.

Table 10. STRAY LIGHT CONCENTRATION EQUIVALENTS (mg/l) FROM CALCIUM[a]

		50 mg/l Ca			200 mg/l Ca			500 mg/l Ca		
		Wavelength relative to analyte line			Wavelength relative to analyte line			Wavelength relative to analyte line		
	λ(nm)	-.04 nm	0	+.04 nm	-.04 nm	0	+.04 nm	-.04 nm	0	+.04 nm
Al	308.22	0.0002	-.0023	0.0035	-.0190	0.0178	0.0258	0.0361	0.0484	0.0511
Al	396.15	0.1397	0.1562	0.1709	0.4968	0.5641	0.6118	1.0862	1.1459	1.2387
As	193.76	0.5582	0.5781	0.3638	1.5179	1.6186	1.3971	2.7688	2.9367	2.4181
B	249.68	0.0036	-.0005	0.0061	0.0125	0.0082	0.0198	0.0389	0.0242	0.0366
Ba	455.40	0.0007	0.0006	0.0007	0.0025	0.0025	0.0027	0.0048	0.0047	0.0050
Be	313.04	-.0039	0.0009	-.0008	0.0001	0.0002	0.0009	0.0002	0.0004	0.0003
Cd	226.50	0.0055	0.0068	0.0022	0.0232	0.0213	0.0189	0.0389	0.0485	0.0366
Co	238.89	0.0091	0.0045	0.0057	0.0262	0.0223	0.0257	0.0534	0.0426	0.0532
Cr	267.72	0.0056	0.0015	0.0022	0.0135	0.0115	0.0191	0.0341	0.0292	0.0306
Cu	324.75	-.0003	-.0001	-.0003	-.0003	-.0002	0.0010	0.0017	0.0027	0.0030
Fe	259.94	0.0219	-.0018	0.0016	0.0047	0.0038	0.0079	0.0112	0.0094	0.0150
Hg	253.65	0.0047	0.0158	0.0301	0.0714	0.0555	0.0761	0.1158	0.1368	0.1571
Mn	257.61	0.0001	0.0001	0.0001	0.0006	0.0003	0.0007	0.0013	0.0012	0.0017
Mo	403.08	0.0037	0.0041	0.0042	0.0156	0.0168	0.0212	0.0417	0.0441	0.0443
Na	287.15	0.0074	0.0050	-.0077	0.0317	0.0239	0.0385	0.0748	0.0719	0.0749
Ni	231.60	0.0162	0.0171	0.0122	0.0476	0.0516	0.0520	0.0914	0.0933	0.0992
Pb	220.35	0.1248	0.0976	0.1248	0.3436	0.3436	0.4023	0.6256	0.5629	0.7277
Pb	405.78	0.0669	-.0079	0.0636	0.2625	0.2388	0.2829	0.6596	0.5355	0.6789
Sb	206.84	0.0991	0.1032	0.1126	0.3218	0.2923	0.3828	0.5313	0.5217	0.7539
Se	196.09	0.2938	0.2388	0.2653	0.8189	0.7842	0.8189	1.4534	1.3211	1.3973
Sn	303.41	0.0029	0.0008	0.0041	0.1002	0.1783	0.2877	0.4774	0.6478	0.6838
Sr	407.77	0.0008	0.0050	0.0050	0.0004	0.0222	0.0004	0.0011	0.0564	0.0018
Ti	334.94	0.0010	0.0018	0.0001	0.0061	0.0048	0.0549	0.0275	0.0391	0.1369
V	292.40	0.0006	0.0002	0.0003	0.0043	0.0035	0.0047	0.0114	0.0094	0.0121
Y	242.22	0.0224	0.0158	0.0145	0.0635	0.0675	0.0661	0.1182	0.1329	0.1342
Y	371.03	0.0000	0.0002	0.0001	0.0005	0.0011	0.0010	0.0025	0.0022	0.0026
Zn	213.86	0.0067	0.0078	0.0042	0.0169	0.0224	0.0181	0.0294	0.0320	0.0287

[a]When the gross (sample) signal level is so low that its uncertainty overlaps that of the blank signal, negative net intensities may occur. Under these conditions the negative values should be of negligible magnitude.

Table II. STRAY LIGHT CONCENTRATION EQUIVALENTS (mg/l) FROM MAGNESIUM[a]

		10 mg/l Mg			40 mg/l Mg			100 Mg/l Mg		
		Wavelength relative to analyte line			Wavelength relative to analyte line			Wavelength relative to analyte line		
	λ(nm)	-.04 nm	0	+.04 nm	-.04 nm	0	+.04 nm	-.04 nm	0	+.04 nm
Al	308.22	-.0282	-.0059	0.0146	0.0017	-.0142	0.0089	-.0029	0.0047	0.0172
Al	396.15	-.0067	-.0075	0.0027	0.0010	-.0067	0.0005	-.0062	-.0010	-.0060
As	193.76	0.0933	0.0933	-.0200	0.2239	0.1493	0.0933	0.3265	0.2544	0.2798
B	249.68	-.0020	-.0026	0.0005	0.0036	0.0025	0.0057	0.0030	0.0025	0.0077
Ba	455.40	-.0000	0.0010	0.0001	0.0001	0.0005	0.0003	0.0005	0.0006	0.0004
Be	313.04	-.0000	0.0002	0.0020	-.0000	0.0001	-.0000	0.0000	0.0002	-.0000
Ca	315.8[a]	0.0015	-.0043	0.0011	0.0023	0.0000	0.0019	0.0035	-.0002	-.0015
Cd	226.50	0.0000	0.0029	-.0005	0.0022	0.0036	-.0003	0.0058	0.0052	0.0006
Co	238.89	-.0043	0.0005	-.0007	0.0019	0.0012	0.0040	0.0038	0.0052	0.0057
Cr	267.72	-.0016	-.0037	0.0031	0.0047	-.0015	0.0021	0.0065	0.0015	0.0051
Cu	324.75	-.0013	0.0008	0.0004	0.0002	-.0037	0.0001	-.0000	-.0003	-.0005
Fe	259.94	0.0001	-.0012	0.0009	0.0019	-.0009	0.0016	0.0027	0.0041	-.0023
Hg	253.65	-.0015	0.0142	0.0031	0.0142	0.0047	0.0301	0.0349	0.0365	0.0380
Mn	257.61	-.0030	0.0009	0.0002	0.0002	0.0005	0.0001	0.0004	0.0006	0.0004
Mn	403.08	-.0036	-.0023	0.0031	-.0018	-.0025	0.0009	-.0013	-.0031	-.0018
Mo	287.15	-.0029	-.0017	0.0113	0.0245	0.0029	0.0223	0.0383	0.0386	0.0481
Ni	231.60	-.0004	0.0044	0.0024	0.0054	0.0014	0.0019	0.0132	0.0167	0.0143
Pb	220.35	0.0420	0.0311	0.0030	0.0545	0.0233	0.0311	0.0858	0.0586	0.0701
Pb	405.78	-.0054	-.0305	0.0471	0.1771	0.0329	0.0471	0.4376	0.2910	0.3542
Sb	206.84	0.0234	0.0157	-.0093	0.0468	-.0093	0.0327	0.0758	0.0703	0.0280
Se	196.09	0.0383	0.0525	0.0143	0.1247	0.0862	0.1391	0.2386	0.1777	0.2115
Sn	303.41	-.0098	-.1036	0.0593	0.0045	-.0038	0.0041	0.0742	-.0197	0.0549
Sr	407.77	-.0009	0.0010	0.0002	-.0000	0.0004	0.0007	-.0000	0.0001	-.0006
Ti	334.94	-.0047	-.0063	0.0058	-.0093	-.0061	0.0005	-.0016	-.0025	-.0005
V	292.40	-.0010	-.0016	0.0010	0.0015	-.0007	0.0016	0.0014	0.0010	0.0023
Y	242.22	0.0039	0.0039	-.0026	0.0118	0.0079	0.0065	0.0227	0.0131	0.0118
Y	371.03	-.0005	0.0004	0.0003	-.0004	0.0004	0.0001	-.0000	0.0010	-.0001
Zn	213.86	0.0020	0.0065	-.0026	0.0038	0.0058	0.0013	0.0029	0.0139	0.0015

[a]See explanatory note for Table 10.

1. secondary optics stray light,

2. a residual impurity of the analyte element in the calcium or magnesium test solution,

3. a spectral line interference from calcium or magnesium.

The first cause is not probable because the exit slit for the Mg 279.55 nm line was blocked for this experiment and no exit slits were present for the strongest calcium lines. An example of a residual impurity is shown by the results for strontium from the 50, 200, and 500 mg/L calcium solutions (Table 10). An example of a spectral line interference is shown by the results for the Pb 405.78 nm line with the magnesium solutions (Table 11). A magnesium line is located 0.019 nm below the lead wavelength.

Spectral line broadening (in the excitation source and from instrumental causes) and shifts in the true spectral background are being investigated on other ICP systems in the Ames Laboratory. The background shifts from these causes are generally small but may become significant as other sources of stray light are reduced or eliminated.

SOLUTION OF STRAY LIGHT PROBLEMS

After the various sources of stray light in the ICPQ polychromator had been identified attempts were made to reduce or eliminate the stray light level or to correct empirically for its effects.

The largest secondary optics stray light signals from magnesium were obtained from the Cr 267.72 and V 292.40 nm channels. The geometrical relationships of these channels with respect to the Mg 279.55 channel are shown in Figure 7. The split peak exhibited by the vanadium profile (Figure 4) suggests that the scattering is greatest when the solid angle of the magnesium radiation is at either edge of the magnesium mirror. Baffles were placed, one at a time, in appropriate locations to block scattering of the magnesium radiation from one component to another. Baffle 1, located as shown in Figure 7, had essentially no effect on the stray light received by the chromium and vanadium channels. Baffle 2, placed to block reflections from the glossy manganese photomultiplier shield, eliminated most of the stray light received by the vanadium channel but had no effect on the chromium channel. Baffle 3 eliminated most of the stray light received by both chromium and vanadium. These experiments indicated that the reflective surface of the magnesium mirror actually transmitted part of the magnesium radiation which then scattered from the back and edge

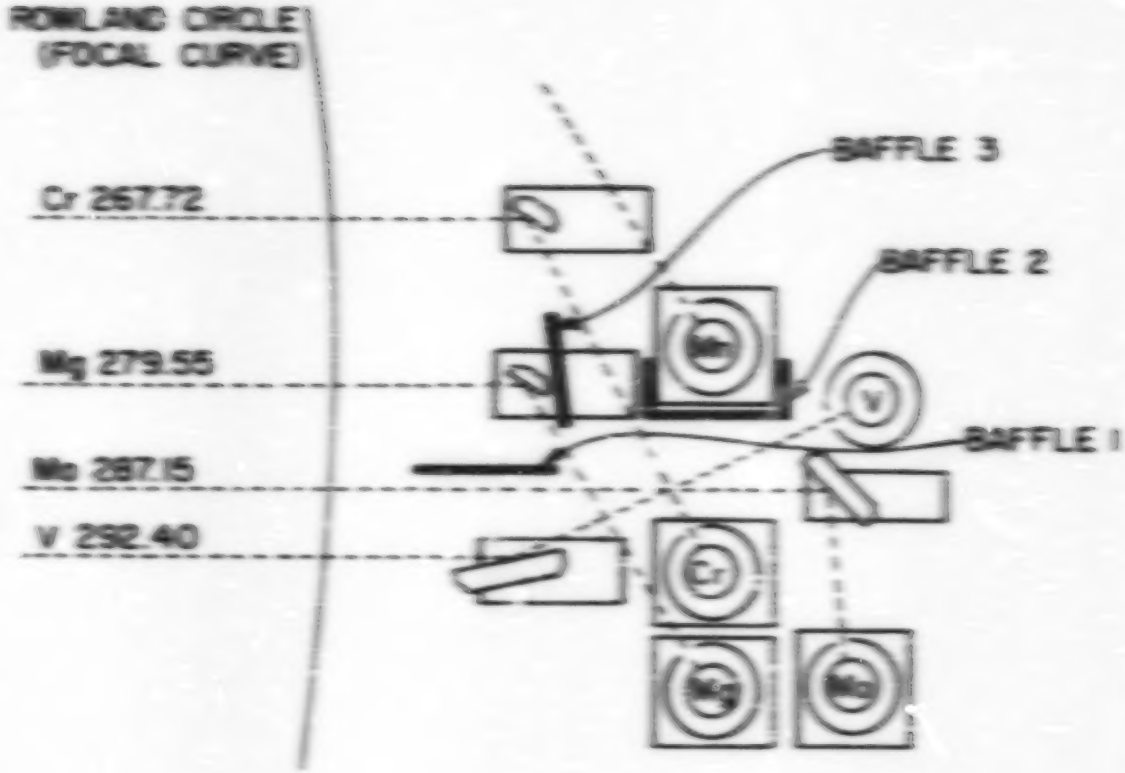

Figure 7. Geometrical arrangement of secondary optics in the region of the Mg 279.55 nm line.

surfaces of the mirror blank to nearby photomultipliers. The reduction in stray light to the vanadium channel by Baffle 7 was due mainly to its blockage of the path to the magnesium mirror rather than to its blockage of reflections from the manganese photomultiplier shield.

A zero-order light trap is located on the low wavelength side of the polychromator case. A flat black paper baffle was added to this trap to prevent a direct reflection of zero-order radiation from passing through a narrow open joint in the trap and reflecting directly to the focal curve. Also, cadmium plated socket-head cap screws on the face of the grating mask were painted with optically flat black paint. Shiny objects at each of the lower corners of the grating (apparently part of the mount) reflected the primary radiation to the grating at an inappropriate angle and the resulting diffracted light appeared as diagonal streaks emanating from the grating. According to advice from ARL a second mask was superimposed on the original grating mask to block this potential source of stray light. Because this mask can be no closer to the grating than about 0.5 cm it may vignette the diffracted rays from the grating for certain wavelengths.

Empirical corrections for stray light were first approached through the interference correction method as provided for in the ICPQ software. In this method a concentration correction factor K is obtained from the product of an interference coefficient B and interferent concentration C_i

$$K = BC_i \qquad (2)$$

where B is the analyte concentration error (caused by the interferent) divided by the interferent concentration and is obtained from a solution containing only the interferent. The real analyte concentration is then obtained by subtraction of the error components (one for each interferent) from the gross calculated concentration. In practice this correction technique over corrected for interferent concentrations greater than and under corrected for interferent concentrations less than that used for the calculation of the interference coefficient. The reason for this failure is illustrated in Figure 8 in which interference coefficients for arsenic, selenium, lead, and antimony are shown as functions of calcium concentration. The curvature correlates quite well with the self-absorption exhibited by the Ca II 393.37 and 396.85 nm lines. Correction coefficients based on intensity rather than concentration should solve the problem. These intense calcium lines exhibit different degrees of self-absorption, however, hence neither line provides the proper base intensity for correction of the background shifts caused by the pair.

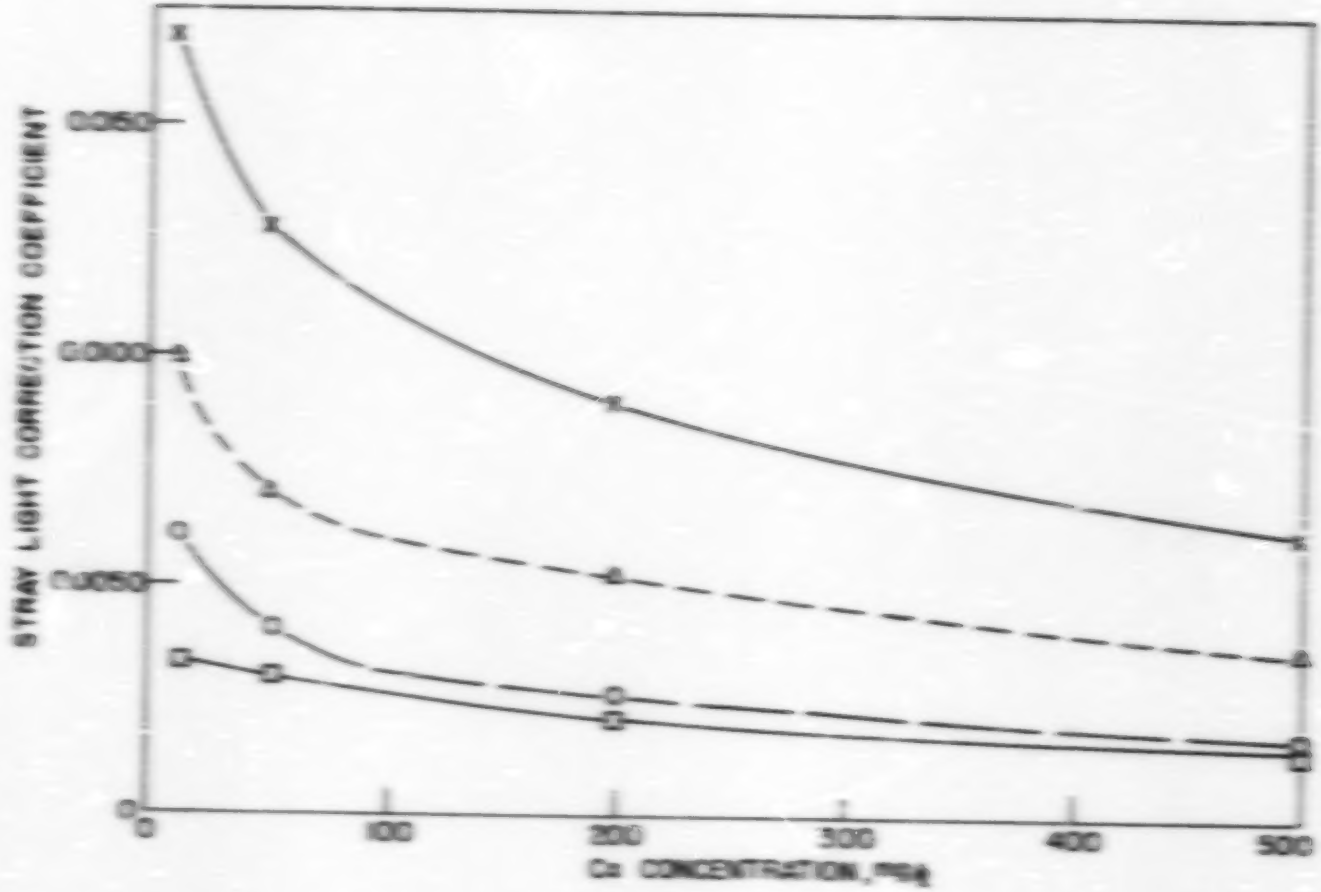

Figure 9. Stray light correction coefficients as a function of calcium concentration.
X As 193.76 nm, △ Se 196.09 nm,
○ Pb 220.35 nm, □ Sb 206.84 nm.

Wavelength profiles, e.g. Figures 2, 3, 4, and 6, have been used extensively for evaluation of stray light problems in real samples and for correction for the effects of background shifts whatever their cause. Often the background level at an analyte wavelength can be established from these profiles, by a line joining the backgrounds at either side of the line.

SECTION 6

DISCUSSION

In general, the basic hardware and software were relatively trouble free in routine operation during the evaluation period. Also, the basic operating routines were easy to learn by personnel who had previous experience with ICP-AES systems. The malfunctions that did occur included: 1) occasional fouling of the nebulizer tip from high salt concentration solutions, 2) slippage of the digital counter assembly on the entrance slit adjustment (profile) screw (the digital counter assembly was also subject to being struck by the outer cabinet upon opening for access to the exit slit-photomultiplier region of the spectrometer), 3) intermittant failure of capacitors to discharge properly on several channels between integrations.

The following section contains general and specific comments about the operation and performance of the system.

DYNAMIC RANGE

The dynamic range of the system is presently limited by the signal measurement system (3-3½ orders of magnitude with standard deviations approximating 1% or less) rather than by the sample excitation system.

DETECTION LIMITS

Recent design improvements have made ultrasonic transducers much more resistant to degradation by corrosive solutions. In general, the ultrasonic technique produces an order of magnitude or more improvement in comparison to detection limits obtained by pneumatic nebulization (14). Similar improvements should be realized on the ICPQ as well as other ICP systems.

SOFTWARE

The PDP 11/03 computer was supplied with 8K of memory. The ARL software used all but about 200 words. Additional routines would require an increase in computer memory. The software as supplied, however, was written to be compatible with all ARL

ICPQ systems having up to 48 channels. The EPA-Athens instrument had 32 channels. Therefore, approximately one-third of the space allocated for data storage was wasted (≈1000 words). This space could be used for calculation of detection limits or interference correction coefficients, or possibly both routines or others could be fitted into this space. For example, computer control of a stepper motor and of the integration sequence for wavelength profiling would be very useful. The economics of changes in the existing software versus purchase of addition memory must be considered, of course.

STRAY LIGHT

As mentioned earlier the stray light problem constitutes the most serious deficiency of the ICPQ system. Stray light levels have been assessed with respect to the more stringent of the EPA criteria levels for public water supplies and continuous use irrigation water (1, 2) and the results are shown in Table 12. Ultrasonic nebulization, with its factor of 10 or better improvement in detection limits, will be of significant help with regard to detectability for all of the elements listed in Table 12 but its greatest value will be for those elements in column III for which pneumatic nebulization presently provides insufficient powers of detection. Ultrasonic nebulization is not expected to influence the relative stray light levels significantly, therefore improvements in the stray light properties of spectrometers is still a high priority objective.

Table 12. CLASSIFICATION OF SPECTRAL LINES WITH RESPECT TO STRAY LIGHT PROBLEMS AS OBSERVED ON QA 137 POLYCHROMATOR

I	II	III
Stray light is a small fraction of signal from EPA criteria level concentration.	Spectral sensitivity is sufficient, but stray light from hard waters could cause significant errors at EPA criteria level concentrations.	Poor sensitivity of the spectral line (with pneumatic nebulization) and stray light are both significant problems at the EPA criteria level concentrations.
Al 308.22	Al 396.15	As 193.76
B 249.68	Co 238.89	Cd 226.50
Ba 455.40	Cr 267.72	Hg 253.65
Be 313.04	Mn 403.08	Mo 202.15
Cu 324.75	Ni 231.60	Pb 220.35
Fe 259.94	V 292.40	Pb 405.78
Mn 257.61		Se 196.09
Zn 213.86		

SECTION 7

PUBLICATIONS

1. Larson, G. F., V. A. Fassel, R. K. Winge, and R. N. Kniseley, "Ultratrace Analyses by Optical Emission Spectroscopy: The Stray Light Problem," Appl. Spectrosc. 30, 384-391, July-August 1976.

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